

Li⁺ ion conduction mechanism in poly (ϵ -caprolactone)-based polymer electrolyte

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Abstract In this work, solid polymer electrolytes based on poly(ϵ -caprolactone) (PCL) with lithium bis(oxalato)borate as a doping salt were prepared by solution cast technique using DMF as a solvent. The electrical DC conductivity and dielectric constant of the solid polymer electrolyte samples were investigated by electrochemical impedance spectroscopy over a frequency range from 50 Hz to 1 MHz. It was found that the DC conductivity increased with increase in the salt concentration to up to 4 wt% and thereafter decreased. Dielectric constant versus salt concentration was used to interpret the decrease in DC conductivity with increase in salt concentration. The DC conductivity as a function of temperature follows Arrhenius behavior in low temperature region, which reveals that ion conduction occurs through successful hopping. The curvature of DC conductivity at high temperatures indicates the contribution of segmental motion to ion conduction. High values for dielectric constant and dielectric loss were observed at low frequencies. The plateau of dielectric constant and dielectric loss at high frequencies can be observed as a result of rapid oscillation of the AC electric field. The HN dielectric function was utilized to study the dielectric relaxation. The experimental and theoretical data of dielectric constant are very close to each other at low temperatures. At high temperatures, the simulated data are more deviated from the experimental curve of dielectric constant due to the dominance of electrode polarization. The non-unity of relaxation parameters (α and β) reveals

that the relaxation processes in PCL-based solid electrolyte is a non-Debye type of relaxation.

Keywords Poly(ϵ -caprolactone) · LiBOB · DC conductivity · Dielectric permittivity

Introduction

The knowledge of polymer electrolytes is a highly specialized interdisciplinary field which encompasses the disciplines of electrochemistry, polymer science, organic chemistry, and inorganic chemistry. This field has attracted the attention of many researchers in both academia and industry, due to its potentially promising applications [1]. Polymer electrolytes which are complexes of solvent-free polar polymers and inorganic metal salts are prepared by dissolving salts in high-molecular-weight polymer hosts. Polymer electrolytes have been studied extensively by researchers because of their potential applications, namely, in high-energy density batteries and fuel cells [2]. The key advantages of solid polymeric electrolytes over liquid electrolytes are good mechanical properties, ease of fabrication to thin films, desirable sizes, and their capability to form proper electrode–electrolyte contact [3, 4]. Polymer electrolytes with sufficiently high room temperature conductivity have attained considerable interest in recent years in the area of polymer research due to theoretical concerns as well as practical importance for the development of electrochemical devices [5]. The choice of a polymer host depends mainly on the presence of polar groups with large sufficient electron donor power to form coordination with cations and a low hindrance to bond rotation [6]. Some polymers are successfully used as a host material to prepare polymer electrolytes for specific applications; among these

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polymers are poly(methyl methacrylate), poly(ethylene oxide), and poly(vinylidene fluoride) [7]. Poly(ϵ -caprolactone) (PCL) is a promising synthetic biodegradable polymer because of its marked degradation in aqueous medium and in contact with microorganisms [8]. Biodegradable polymers have attracted much attention in biomedical application [9]. Previous studies [2] have shown that PCL can be used as a polymer matrix for the preparation of polymer electrolytes due to the existence of carbonyl functional groups in its backbone structure. Thus, the ability of PCL as a host polymer is due to the presence of carbonyl groups in its structure that can dissolve inorganic salt as a result of electrostatic interaction. Fonseca et al. [8], for the first time, prepared the PCL:LiClO₄-based polymer electrolyte for rechargeable batteries. Due to its low cost, low toxicity, stability, and ease of preparation, lithium bis(oxalato)borate (LiBOB) is currently being evaluated as a suitable salt for use in lithium ion battery technology [10]. Also compared with other Li salts, LiBOB salt has low lattice energy making it more suitable to participate in the formation of polymer electrolytes [10, 11]. Ionic transport in polymer electrolyte is, however, not completely understood and remains an obstacle to achieving the required ambient conductivity [12]. Electrochemical impedance spectroscopy (EIS) has been used as a powerful technique to study the electrical properties of materials such as double-layer capacitance, diffusion layer, and charge transfer resistance [13]. Dielectric relaxation and ion conduction mechanism in solids are the most intensively researched topics in condensed matter physics [14]. Particularly, the study of dielectric relaxation in solid polymer electrolytes is a powerful approach for obtaining information about the characteristics of cation–polymer interactions, and the dielectric constant plays a fundamental role which shows the ability of the polymer material to dissolve salts [15]. Electrical impedance studies of polymers reveal some structural details and add valuable complementary information to the electrical application of polymer materials [16]. Thus, the study of DC conductivity and dielectric permittivity (ϵ) is important to understand the ion conduction mechanism in polymer electrolytes. In view of the above statements, the main objective of the present work is to investigate the ion conduction mechanism in PCL as a polymer host and LiBOB as a doping salt by EIS.

Experimental

Materials and methods

Poly(ϵ -caprolactone) with $M_n = 80$ kDa from Sigma-Aldrich (USA) and LiBOB with $M_w = 193.79$ g/mol from Sigma-Aldrich (USA) were used as raw materials in this

Table 1 Composition of PCL:LiBOB polymer electrolytes

Designation	Poly(ϵ -caprolactone) (g)	LiBOB (wt%)	LiBOB (g)
PE1	1.0	1.0	0.0101
PE2	1.0	2.0	0.0204
PE3	1.0	3.0	0.0309
PE4	1.0	4.0	0.0416
PE5	1.0	5.0	0.0526

work. The solid polymer electrolyte (SPE) films were prepared by the solution cast technique with *N,N*-dimethylformamide (DMF) as a solvent. To prepare the samples, 1 g of PCL was fixed and dissolved in DMF solvent. To this system, LiBOB salt was added and varied from 1 to 5 wt% in steps of 1 wt% to prepare various compositions of PCL:LiBOB polymer electrolytes. The mixtures were stirred continuously until homogeneous solutions were obtained. After casting in different Petri dishes, the solutions were left to dry at 50 °C. The films were transferred into a desiccator for continuous drying. This procedure produces a solvent-free film. Table 1 shows the concentration of the prepared samples.

Complex impedance spectroscopy

The complex impedance spectroscopy is widely used to characterize the electrical properties of the materials. The impedance of the films was measured using the HIOKI 3522-01 LCR Hi-tester (Japan) that was interfaced to a computer in the frequency range from 50 Hz to 1,000 kHz. The software controls the measurements and calculates the real and imaginary parts of the impedance. The SPE films were cut into small discs of 2 cm diameter and sandwiched between two stainless steel electrodes under spring pressure. The complex impedance parameters (i.e., real (Z') and imaginary (Z'') components of impedance) were used to calculate the DC conductivity (σ_{dc}), dielectric constant (ϵ'), and dielectric loss (ϵ'') using the following relations,

$$\sigma_{dc} = \left(\frac{1}{R_b} \right) \times \left(\frac{d}{A} \right) \quad (1)$$

$$\epsilon' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \quad (2)$$

$$\epsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} \quad (3)$$

where d is the thickness and A is the area of the film. C_0 is vacuum capacitance of the cell and is equal to $\epsilon_0 A/d$, where ϵ_0 is the permittivity of the free space and $\omega = 2\pi f$, in which f is the frequency.

Results and discussion

Composition dependence of σ_{dc} and ϵ'

Figure 1 shows the conductivity of PCL films with various LiBOB salt contents at room temperature. It can be seen that the DC ionic conductivity of the PCL-based electrolyte increased with increasing LiBOB concentration up to 4 wt%. It was observed that conductivity values increased by more than five orders of magnitude from $1.79 \times 10^{-11} \text{ S cm}^{-1}$ for pure PCL film to $6.50 \times 10^{-6} \text{ S cm}^{-1}$ for PCL film containing 4 wt% of LiBOB salt. The reported conductivity by Ohki et al. [17] for pure PCL is very close (similar order) to that obtained in our study. The maximum DC conductivity reported by Fonseca et al. [8] was $1.2 \times 10^{-6} \text{ S cm}^{-1}$ for PCL complexed with 10 wt% LiClO_4 at room temperature, which is comparable to that obtained in this work (for PCL film with 4 wt% LiBOB).

The increase in conductivity is attributed to the increase in the number density of mobile ions provided by the salt. According to Liang et al. [18], the salt can be completely dissociated at low concentration, and thus the number of mobile ions which participate in DC conductivity increases with increase in salt concentration. Similar behavior of DC conductivity with salt concentration was reported by Fonseca et al. [19] for PCL:LiTf polymer electrolyte. The decrease in DC conductivity at 5 wt% can be ascribed to ion association. Ion conduction in polymer electrolytes is quite difficult to understand. The dissolved ions can associate into ion pairs, triplets, and larger aggregates. The formation of neutral ion pairs can weaken the electrical conductivity. Thus, it is important to detect and study such entities. The ion pairs have a permanent dipole moment, which is stronger than that of the other types. Because the host polymer has a comparably low dielectric constant, the ion pairs can be detectable in dielectric measurement [20]. Hence, the study of dielectric constant can be used to investigate and interpret the conductivity behavior of polymer electrolytes.

From the above discussion, it is understood that the dielectric study can be used to detect the conductivity behavior of polymer electrolytes. The physics behind the relationship between DC conductivity and dielectric constant can be explained as follows. The general expression for conductivity is:

$$\sigma = \sum nq\mu \quad (4)$$

where n is the charge carrier density, q is $1.6 \times 10^{-19} \text{ C}$, and μ is the mobility of the ions. Thus, the rapid increase in DC conductivity for the salt concentration from 1 to 4 wt% can be explained by an increase in either ionic mobility or concentration of charge carriers, but the latter is preferred because more salt is added.

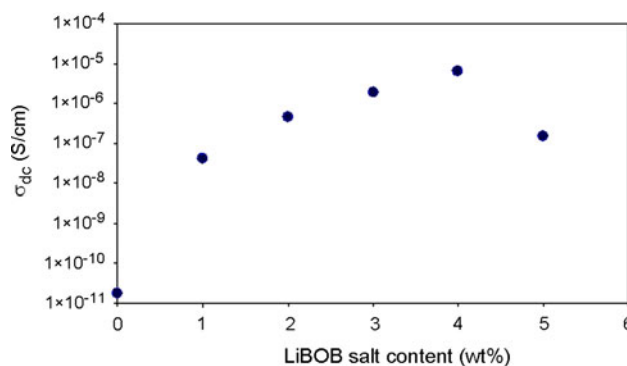


Fig. 1 DC ionic conductivity of PCL films at various concentrations of LiBOB salt

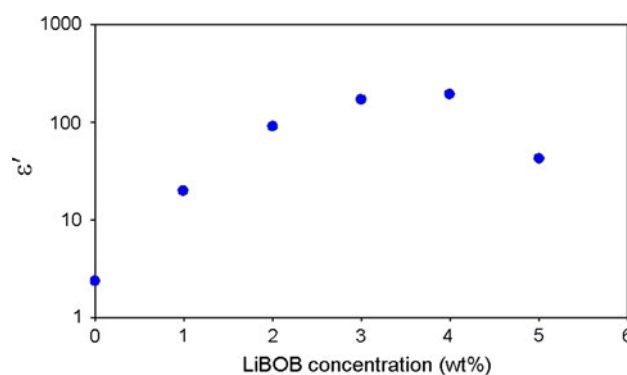


Fig. 2 Composition dependence of dielectric constant (at 1 kHz) for PCL films as a function of LiBOB concentration (wt%) at room temperature

It is important to notice that the carrier density is directly related to the dissociation energy U and dielectric constant ϵ' , which can be understood through this relation ($n = n_0 \exp(-U/\epsilon'KT)$). The increase in the value of dielectric constant with salt concentration indicates that there is an increase in charge carrier concentration and hence an increase in DC conductivity [21].

Figure 2 shows the variation of dielectric constant versus salt concentration. It is obvious that this dielectric constant variation against salt concentration follows the same trend as observed for DC conductivity correlation with salt concentration (Fig. 1). Thus, the room temperature study of DC conductivity and dielectric constant as a function of salt concentration indicated the powerful ability of dielectric spectroscopy to study the conductivity behavior of solid polymer electrolytes.

Temperature dependence of σ_{dc} and ϵ^*

Figure 3 shows the variation of DC conductivity as a function of reciprocal temperature for PCL–LiBOB

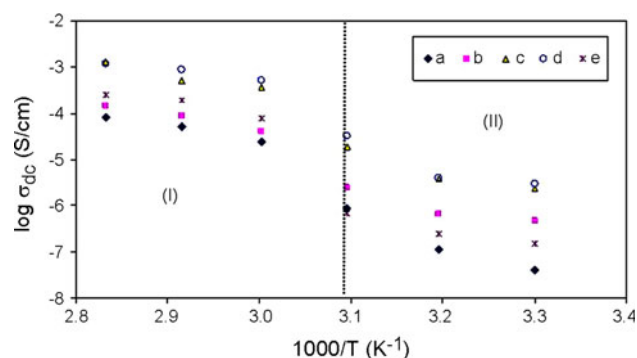


Fig. 3 Temperature dependence of ionic conductivity of PCL:LiBOB films for (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5 wt% of LiBOB salt

polymer electrolytes. It can be seen that the DC conductivity increased with increasing temperature. The overall conductivity versus $1,000/T$ can be separated into two regions for all solid electrolyte samples (Fig. 3). The first region (region I) follows the Arrhenius behavior from 303 to 323 K and the second region (region II) follows the VTF behavior from 323 to 353 K, with a rapid increase in conductivity. A slow rate of increasing DC conductivity in region I may be due to the hopping of mobile ions thermally, while the fast rate of rise in DC conductivity in region II can be linked to the phase transition of the electrolyte system from semi-crystalline to amorphous [22].

The appearance of curvature in DC conductivity at 323 K reveals the decrease in melting temperature ($T_m = 329$ K) of PCL [8] as a result of complexation between the PCL and LiBOB salt. It was reported that high ionic conductivity can be observed above the melting temperature (T_m), as obvious in Fig. 3, in which the amorphous concentration was higher than the crystalline region. Above T_m , the connected network of amorphous regions can provide fast ion conducting pathways leading to the enhancement in ion mobility and consequently yield a high ionic conductivity [23].

The temperature-dependant curvature (region II) reveals that the PCL–LiBOB electrolytes obey the Vogel–Tammann–Fulcher (VTF) behavior, i.e., region II can be interpreted in terms of the VTF model. The VTF model suggests that ion conduction follows free volume model and is dependent on segmental motions of the polymer. As temperature increased, the amorphous phase expanded due to the phase transition of the electrolyte system and produced free volume around polymer chains. Thus, ion solvated molecules or polymer segments can move into the free volume. The resulting conductivity is represented by the overall mobility of ion and polymer, which is determined by the free volume around the polymer chain. The larger the free volume, the greater is the ability of the chain to rotate; hence, ions can transport more rapidly [24].

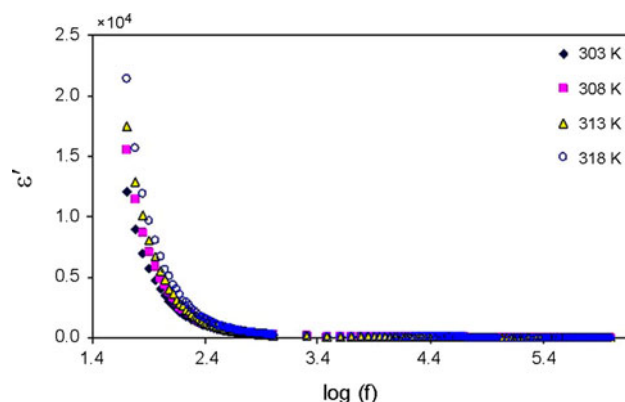


Fig. 4 Frequency dependence of dielectric constant at different temperatures for PCL:LiBOB electrolyte (4 wt% LiBOB)

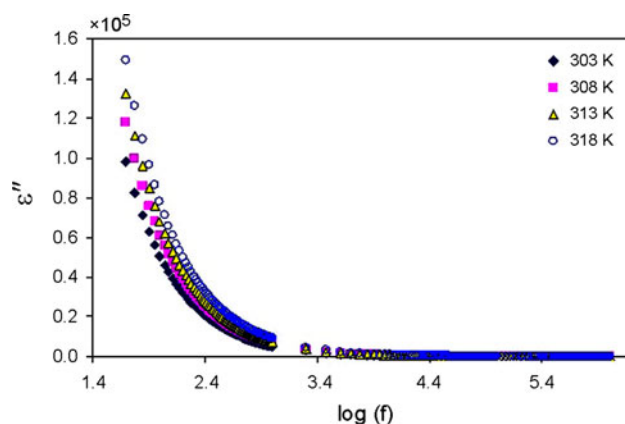


Fig. 5 Frequency dependence of dielectric loss at different temperatures for PCL:LiBOB electrolyte (4 wt% LiBOB)

Figures 4 and 5 show the frequency dependence of dielectric constant and dielectric loss at different temperatures for the highest conducting PCL:LiBOB sample (4 wt%). From these figures, it is seen that both dielectric constant and dielectric loss decrease with increasing frequency, but increase with increasing temperature. At all temperatures, high values of ϵ' and ϵ'' were observed at low frequencies, but at higher temperatures and frequencies became relatively constant. The higher values of ϵ' and ϵ'' can be ascribed to the accumulation of charged species at the electrode/electrolyte interface [25].

The variation of dielectric constant versus temperature is different for non-polar and polar polymers. For non-polar polymers, dielectric constant is generally independent of temperature. But in the case of polar polymers, the dielectric constant increases with the increase of temperature. This behavior can be ascribed to the fact that the orientation of dipoles was facilitated with the rise in temperature and thus permittivity increased [26]. At high

frequencies, there was no excess ion diffusion in the direction of the field due to the fast periodic reversal of the electric field. Thus, polarization due to charge accumulation decreased and led to the decrease in the values of ε' and ε'' , which were almost constant as depicted in Figs. 4 and 5 [27].

The higher value of dielectric loss ($\sim 10^5$) at lower frequencies was due to the free charge motion (DC conductivity) within the material. These values do not correspond to the bulk property of the material, but only due to the “free” charge buildup at the electrode–electrolyte interface. At low frequencies, there was enough time for the charges to build up at the interface before the electric field was reversed and contributed to a large apparent value of ε'' . With increasing frequency, there was no time for the buildup of charges at the interface, but only for the buildup of charges at the boundaries of conducting species in the material and at the ends of conducting paths. This phenomenon led to the so-called conductivity relaxation [28].

The dielectric relaxation study in polymer electrolytes is a powerful approach for understanding the ionic transport properties and relaxation behavior of these materials [29]. The dielectric loss spectra can be further studied by

applying the well-known Havriliak–Negami (HN) function [30] as follows,

$$\varepsilon^* = \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^\beta]^\alpha} \quad (5)$$

where $\Delta\varepsilon$ is the dielectric relaxation strength, τ is the relaxation time, ω is the angular frequency, i is the imaginary unit, and α and β are fractional parameters. Both α and β are between 0 and 1. The experimental values of dielectric loss (ε'') at 303, 308, and 313 K were simulated by the HN equation as shown in Fig. 6. It can be seen that the experimental and simulated data are well fitted at high frequencies. However, at low frequencies the simulated data deviated from the experimental data. The values of α and β are listed in Table 2 for PCL:LiBOB (4 wt% of LiBOB).

The α and β exponents are usually referred to as measures of symmetry and asymmetry of relaxation [31]. The deviation of α and β values (Table 2) from unity reveal the non-Debye relaxation in the PCL:LiBOB system [32]. Understanding the relationship between α and β parameters is important. The α and β exponents are dependent on temperature (Table 2) and other physical parameters of the system under study. However, there is no complete

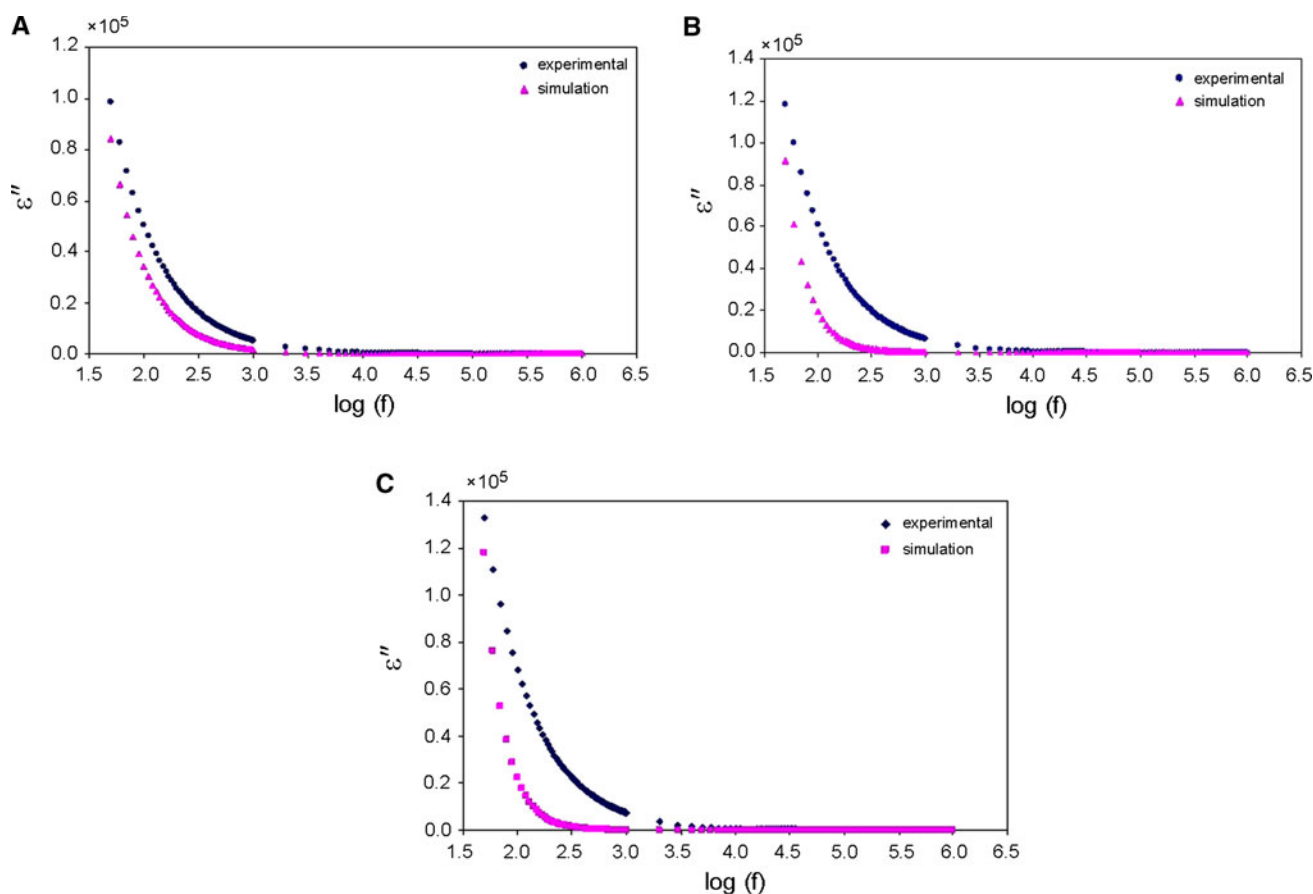


Fig. 6 Experimental and simulated data of dielectric loss (ε'') for PCL:LiBOB samples (4 wt% LiBOB) at **a** 303 K, **b** 308 K and **c** 313 K

Table 2 Values α and β at different temperatures for PCL:LiBOB (4 wt% of LiBOB)

Temperature (K)	α	β
303	0.1	0.2
308	0.4	0.6
313	0.5	0.7

understanding of these dependencies for the time being [31]. It can be noticed that with increasing temperature the simulated data deviate more from the experimental data. This can be ascribed to the increase of charge carrier motion and DC conductivity contribution. Similar behavior was reported by other researchers for polymer blending based on PVA:chitosan [32].

Conclusion

The electrical properties of PCL:LiBOB solid polymer electrolytes have been characterized by EIS. The behavior of DC conductivity and dielectric constant with LiBOB salt concentration revealed that DC conductivity was strongly dependent on the dielectric constant. Extra research is required to show the validity of the relationship between DC conductivity and dielectric constant. The Arrhenius behavior of DC conductivity at the low temperature region is due to ion hopping. The VTF manner of DC conductivity at high temperatures revealed the chain mobility contribution to the conductivity. A high value for the dielectric constant and dielectric loss at low frequencies can be ascribed to electrode polarization (electrical double-layer capacitance). The plateau of dielectric constant and dielectric loss at high frequencies can be observed as a result of rapid oscillation of the AC electric field and thus the Li^+ ions could not follow them due to ion mass inertia. The non-unity of α and β exponents reveals that the dielectric relaxation in PCL-based solid electrolyte is a non-Debye relaxation process due to the distribution of relaxation times.

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